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TOPICAL REPORT

LABORATORY APPARATUS AND OPERATING PROCEDURES FOR DETERMINING THE LONG-TERM ENVIRONMENTAL FATE OF EOR CHEMICALS AND OTHER WASTE FLUIDS

by

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FOREWORD

This document was prepared by the National Institute for Petroleum and Energy Research (NIPER) to fulfill requirements stated under Task 5, Milestone A, Project BE3A, EOR Environmental Compatibility of the FY85 Annual Research Plan.

ABSTRACT

The objective of NIPER's EOR Enviromental Compatibility project, BE3A, is to determine the compatibilities and potential long term environmental effects of EOR chemicals and injected waste fluids with reservoir fluids and rocks. To aid in this effort, a coreflooding system and injection/analysis procedures were designed. The system consists primarily of a Bureau of Mines stainless steel autoclave, or optional Hassler holder, pumps, and associated hardware. The system uses proven core flooding techniques. This report describes the apparatus and procedures involved in performing the research.

MODEL DESCRIPTION

Physical

A laboratory model was designed to study long-term degradation effects of EOR or other waste fluids on reservoir rock or outcrop core material. The model consists of a core flood system of which the primary component is a Bureau of Mines stainless steel autoclave, or core holder, as shown in Figures 1 and 2. Associated pumps, tubing, and gauges were added to facilitate injection and withdrawal of samples (Fig. 3). Figure 2 illustrates the main feature of the core holder, as it relates to this study; namely, that the core and sleeve with end pieces intact may be removed from the autoclave, capped, and stored, allowing multiple cores to be used with one holder and pumping system. During a core flood, the core mounting assembly is submerged in the water-filled autoclave and overburden pressure, to confine the sleeve tightly to the core, is applied by a hydraulic hand pump. Injection ports for overburden as well as sample injection and withdrawal are provided; stainless steel tubing with Swagelok fittings is used.

Experimental

A summary of the experimental model is presented here; detailed test procedures are given in the next section. The program is designed to allow observation of changes within an injected fluid in core material over an extended time. Basically, the method consists of injecting fluid under study into the selected core material, storing the core, and periodically withdrawing and analyzing a sample. The researcher may choose the duration and time increments of the experiment to fit his particular situation. For example, a fluid may be sampled every 1-2 months for 6 months, a year, or until successive analyses are essentially the same. Many cores may be used with a minimum of equipment, and little laboratory time is required for the periodic sample withdrawals. In the case where EOR fluids are studied, the chemical will probably be a sulfonate and/or biocide (1). The procedures were written with this in mind, however, it is possible that with other fluids the sample analyses may be less complicated.

There are two versions of the experimental procedure. The reason for this originates in the fact that when each sample is withdrawn, (approx 5 ml, or 5-10% pore volume in our particular case) an equal volume of injected sample must go into the core to take its place. The injected sample is of course from the original mixture which will have been stored along with the core, however, it will not have actually seen the core material for the same length of time as the sample already in the core.

Version 1 overcomes this possible objection by preparing multiple identical cores at the outset and sampling each core only once at predetermined intervals. The drawbacks to are: 1) the <u>believed</u> identicality of the suite of cores, 2) the length of the experiment must be predetermined, to some extent, rather than based on the results as they are obtained, and, chiefly, 3) the quantity of cores required to test one fluid.

This could be especially troublesome if actual reservoir cores are to be used, in which several core plugs must be butted together to make one 10" core.

Version 2 uses one core per experiment. It assumes that, since the sample size is only 5-10% pore volume and is of the same age as that which is in the core, that the dilution factor would be negligible. In addition, since the withdrawn sample would always exit from the opposite side of the core from the injected fluid, it would require an experiment of more than six time increments (½ to 1 year) in duration for the samples to comingle, at which time the "fresh" sample would have had opportunity to degrade also. One would expect, if a chemical was degrading in a core, significantly more than 5-10% difference, which is the most the dilution factor would cause, in the analyses.

The researcher should decide which time increments, chemicals, and version of the method meets his particular needs. The instructions for executing the experiments were composed with EOR chemicals and version 2, one core per fluid, in mind.

PROCEDURES

A. Low pressure conditions. (May also be used for slightly elevated temperatures (100°-120° F) if desired)

1. Choose chemical to be studied. Choice is based on previously determined priority list.
2. Mix chemical to field use specifications. Add biocide if used.
3. Cut and/or drill core to size. (10" by 1½" diam. cores are used in NIPER equipment).
4. Steam clean core to remove impurities which may interfere with the test. (This step may be omitted if it is felt that steaming would interfere with the test to a greater extent.) Any core steamer is sufficient; ours is simply a rack positioned above a reservoir of water heated by an electrical heating element, all enclosed in a stainless steel box. Experience has shown that 24 hrs in the steamer, followed by 4 hrs drying at approx 200° F is sufficient for outcrop core such as Berea or Cottage Grove.
5. Dry core. (see end of step 4)
6. Allow core to cool to room temperature. If pore volume is to be obtained, weigh core. Although pore volume should not be needed for this experiment, it usually pays to obtain it in the course of the work in case it is needed later on.
7. Saturate core with solution to be studied using vacuum apparatus, see figure 4. The following is a commonly used technique:
   a. place core in lucite holder
   b. evacuate with vacuum pump (30 minutes)
   c. introduce liquid, submerging core
   d. when bubbles stop emanating from core, turn off pump
   e. slowly return the pressure to atmospheric
   f. leave submerged for approximately 1 hour

   Note: Cold trap using liquid N_2 is installed between core and vacuum pump to protect pump (figure 4).
8. Place sleeve in Hassler holder with overburden port connected to house vacuum. Expand against inside of holder by turning on vacuum.
9. Place sheet of teflon or Saran* wrap, 11" x 9.5", on bench.

10. Remove core from lucite holder, quickly drain excess liquid, weigh, and wrap in teflon or Saran sheet.
11. Place wrapped core in Hassler holder, and place end pieces against core. Teflon sheet will overlap enough to cover end pieces. Brush on Pliobond* or equivalent sealant over end pieces and remove vacuum, allowing sleeve to collapse around core. Cap end pieces using Swagelok* caps.
12. Allow Pliobond to cure overnight.
13. Remove end caps and attach core to end plate and tubing assembly via fittings.
14. Place core and sleeve assembly in core holder, which is filled with water. When end cap is tightened, water should overflow out the overburden pressure fitting. Apply overburden pressure with hydraulic hand pump; maintain at about 100 psi over core pressure.
15. Withdraw approximately 5 ml of sample from outlet of core by injecting solution at inlet. (Pump has been hooked to inlet tubing; excess chemical being studied has been saved, stored, and will continue to be stored in order to accomplish future injection/withdrawals. Solution will also be used as a control to compare with analyses of core effluent samples.) Version 1 will not require repeated injection into the core, but rather, the repeat of steps 3-14 for as many time increments as are chosen, for example, six.
16. The initial "time zero" sample withdrawn from the core should be analyzed, along with the control sample from the inlet reservoir bottle, as a baseline for future comparisons. Liquid chromatography can be used for sample analysis. Although the petroleum sulfonates are so complex that total analysis is virtually impossible, chromatograms of the baseline samples may be compared to those of samples taken at later intervals to determine if degradation takes place and possibly into which compound groups the resultant products fall. Also, biocides and pure sulfonates, such as alpha-oelfin sulfonates used in steamflooding operations, are not as difficult.

*Use of product brand names is not an endorsement.

17. After withdrawing sample (step 15), remove core mounting assembly from holder, remove tubing from core, and quickly cap core end pieces with Swagelok caps. (The intent of this and other activities designated to be done quickly (steps 10 & 11), is of course to ensure that air does not enter the core).
18. Core may now be stored until time interval elapses and the next sample is desired, at which time the above withdrawal process will be repeated. If a slightly higher temperature test was desired for comparison, a duplicate core could at this time be stored in an oven at, for example, 100° F. (Version 1 would require a duplicate suite of cores).
19. Process may be repeated as often as results suggest or as time or other constraints permit. Presumably, when successive analyses are essentially the same, the test should be complete.

Alternate or Subsequent Procedure

An alternate procedure, or one that could be used next in sequence, would be to initially saturate the core with a connate brine formulated to compare with that of the reservoirs in which the sulfonate would be used. Chief ingredients of the brine would probably be Ca^{++}, Mg^{++}, and NaCl. The experiment would be carried out much the same way as before, but the brine would be used to displace the initial sulfonate slug injected into the core, whenever a sample was withdrawn.

A one-pore-volume sulfonate slug would be injected into the core at the start of the experiment, after which the experiment would proceed as above. As before, the biocide would be injected with the sulfonate solution. It will prevent bacterial degradation, and itself be analyzed for degradation products.

High Pressure and Temperature

Test procedures for elevated pressure experiments would be the same as for ambient conditions, except in the physical handling of the equipment. Because the core and sleeve must remain under pressure, they must remain in the holder at all times, precluding multiple core analysis with one system. However, using a Hassler holder, available at much less cost than the Bureau

of Mines autoclave, the work could be done. Each core investigated under pressure would be stored in the holder, and hooked up to the pumping system when samples are to be withdrawn.

Presumably temperatures approaching 200° F or more could be handled with this system, with no changes in procedure other than raising the oven temperature, since the entire holder and core would be stored. Temperature limits on the sleeve would be the limiting factor.

Version 1 would be at a disadvantage here due to the multiple holders required.

REFERENCES

1. Collins, A. Gene and Marshall B. Kayser. State of the Art Report with Respect to Interactions, Compatibilities, and Long Term Fate of Injected EOR Fluids and/or Waste Fluids with Reservoir Fluids and Rocks. Topical Report NIPER-70, 1985.

EQUIPMENT LIST

1. Ambient Conditions

- o Bureau of Mines stainless steel autoclave and core mounting assembly
- o Chemical injection pump, type not critical
- o Overburden pump, type not critical
- o Vacuum pump
- o Lucite or plexiglass container for use with vacuum pump to saturate core
- o Associated tubing, vac hose, for use with core saturation apparatus
- o Cold vapor trap and liquid N_2 container for vacuum pump protection if possible
- o Teflon flow lines
- o Swagelok fittings and valves
- o Pressure gauges for core and overburden pressures.
- o Rubber sleeve material
- o Sample containers (flasks, vials)

2. Elevated Temperature/Pressure

For these conditions, stainless steel tubing and fittings should be used, along with sleeve material strong enough to meet specifications. Since the cores must be stored in their holders under pressure, the less-expensive Hassler type would probably be chosen, though not required. An oven of proper size should be available for elevated temperature work.

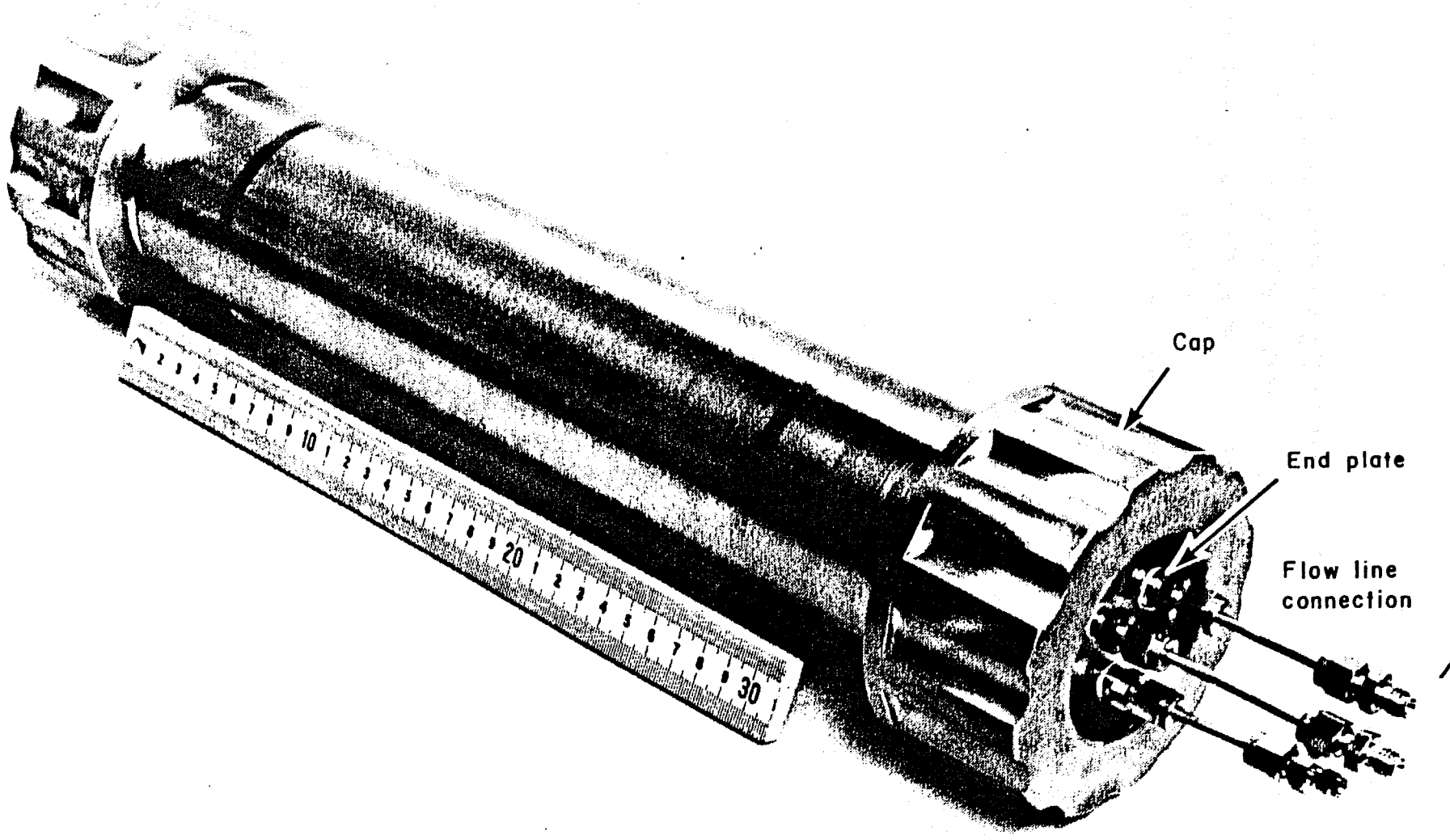

FIGURE 1. - Stainless steel autoclave

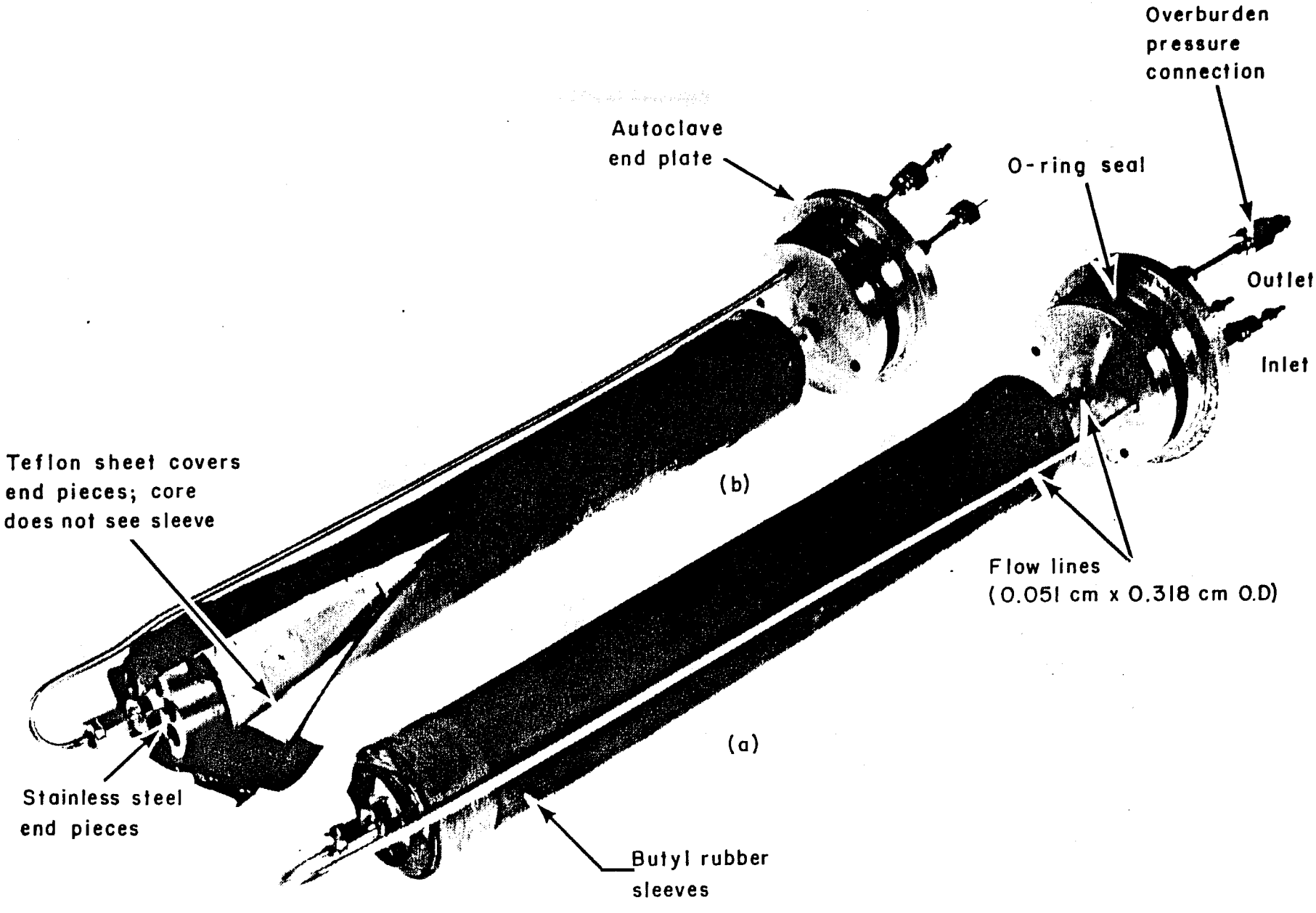

FIGURE 2. - Detail of core mounting assembly.

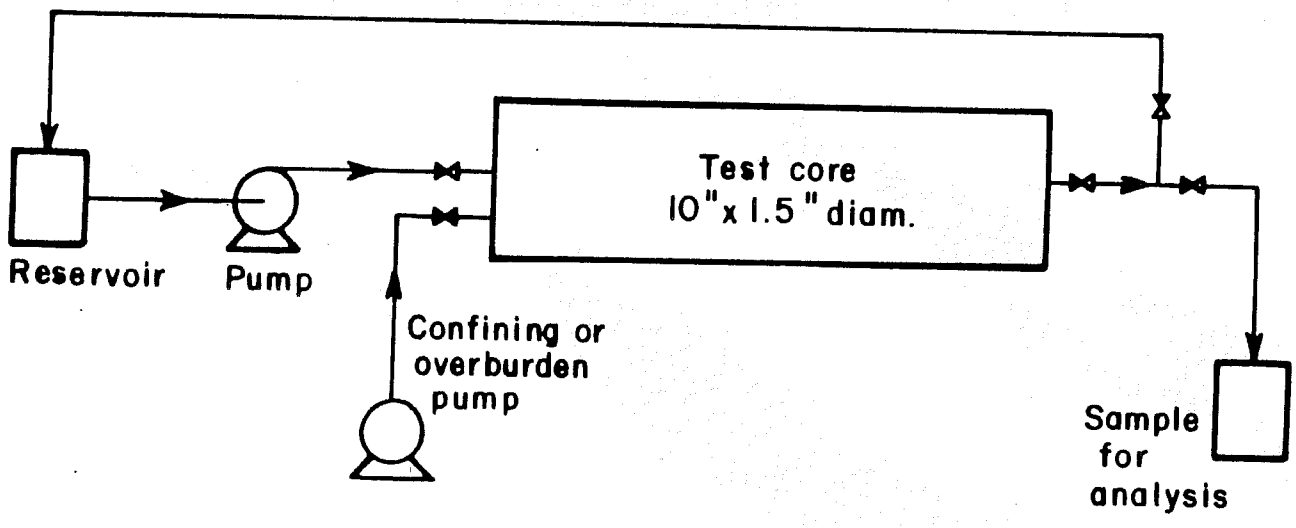

FIGURE 3. - Schematic of laboratory model for long-term degradation studies.

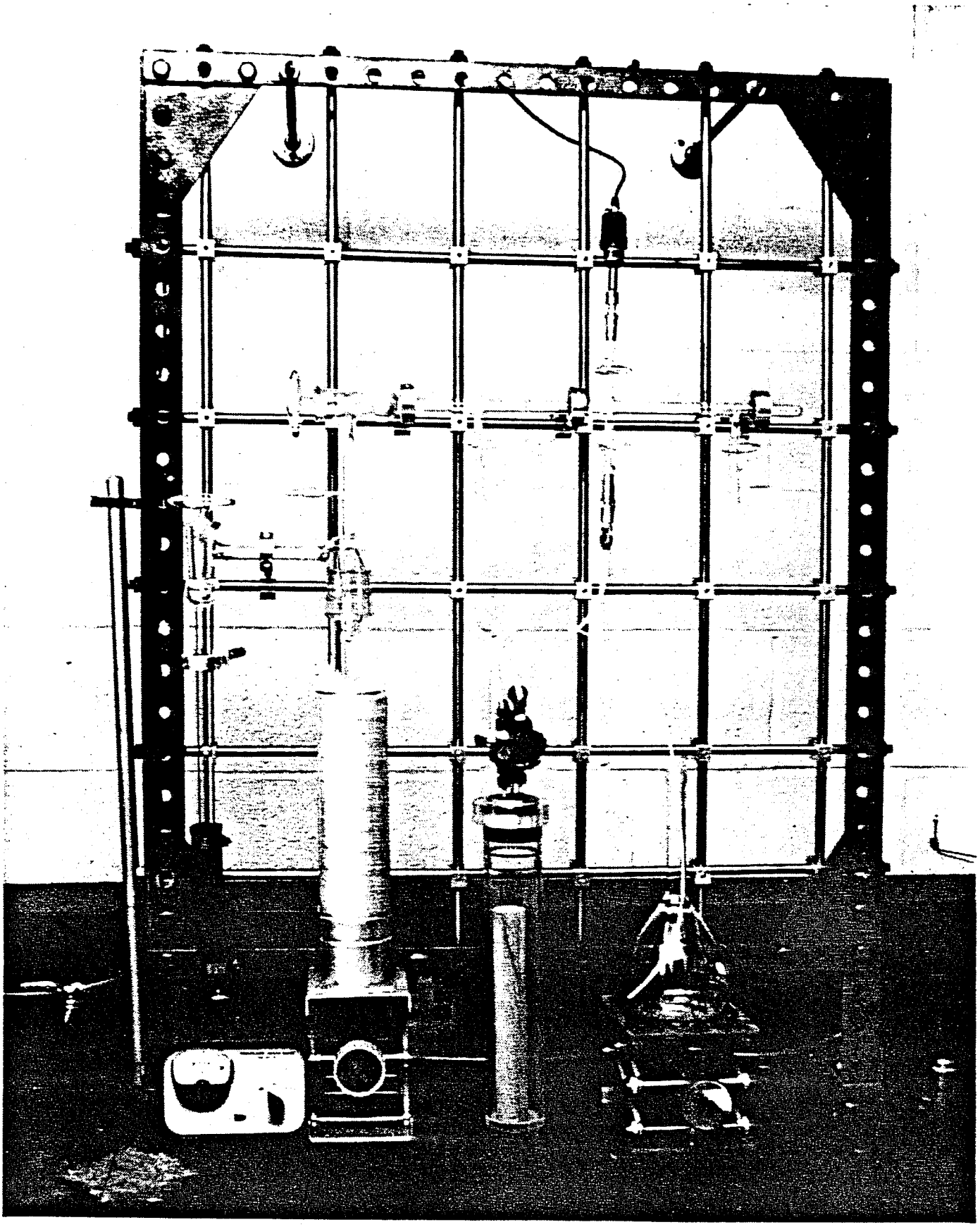

FIGURE 4. - Core saturation apparatus